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**SOLID AQUEOUS GEL COMPRISING A HYDROPHILIC GELLING
AGENT AND A SPECIFIC POLYETHYLENE GLYCOL, COMPOSITION
COMPRISING THIS GEL AND USES**

The present invention relates to a solid aqueous gel, to a solid composition with a continuous aqueous phase comprising such a gel, and to the use thereof in the cosmetic field, especially for making up the skin and/or mucosae and/or keratinous fibers.

Products presented in solid form are known within the cosmetics industry. Products of this type that may be mentioned include, for example, in the makeup field, lipstick, foundation or eyeshadow sticks; in the skincare or lipcare field, lip repair pencils and depigmenting, makeup removing or moisturizing sticks; and, in the hygiene field, deodorant sticks and foaming sticks or bars for shaving or for washing the skin.

It is in effect particularly useful to have available products in stick form, insofar as such products are very convenient to use and are readily portable, with no risk of the product running.

Moreover, makeup products are formulated, very generally, on the basis first of a fatty phase, for reasons of comfort and softness, and secondly of a pulverulent phase, which provides the desired color. This pulverulent phase may comprise pigments and/or fillers and/or nacreous substances. The fatty phase

generally comprises waxes and/or oils and/or pastelike compounds.

However, sticks formulated on a wax basis have certain disadvantages; they have a greasy 5 character, which is not appreciated by users, and they lack freshness on application. Moreover, it is difficult to introduce active hydrophilic substances into them.

To an increasing extent, therefore, attempts 10 are being made to produce makeup sticks comprising an aqueous phase in as high a concentration as possible. However, the sticks comprising a notable aqueous phase are sometimes subject to problems of stability and of 15 lack of cohesion. In particular, these gels, which are produced starting from the combination of a hydrophilic gelling agent and water, have the disadvantage of being fragile and are very liable to break during use.

One means of improving the solidity of the 20 gels is to increase the concentration of hydrophilic gelling agent, but in that case the gels develop cleaving difficulties, i.e., the amount of material removed when the product is taken is inadequate.

However, a prerequisite for a makeup product in particular is that the product can be dispensed 25 optimally, i.e., that it is possible simply, with the aid of the finger or of a sponge or even directly on the skin of the body, for example, not only to take the

appropriate amount of product (not too much, so as not to waste the product, but sufficient to provide a makeup effect) but also to preserve the integrity of the product at the time at which it is dispensed: what 5 is needed is not to break the product as a result of a shearing phenomenon but instead to dispense the entirety of the product, together with the pigments and/or nacreous substances, and/or the fillers if present, which provide the makeup function. Only if 10 this condition is met is it possible to apply the product homogeneously and to obtain a uniform application of makeup.

Cleavable products also exist, but are then too soft and end up by shearing in the course of 15 repeated applications, or else exhibit phenomena of syneresis over the course of time, i.e., the liquid part ends up by exuding and the product presents two phases: an uncleavable solid phase and a liquid phase. The product is no longer able to fulfill its function, 20 namely that of making up, since it is impossible to dispense the pigments on the finger or on a sponge.

Therefore, there is a need for a solid aqueous gel which can be utilized by direct application to the skin or using a sponge, which cleaves well while 25 remaining sufficiently solid, and which does not break during use.

The applicant has unexpectedly discovered that, by combining a hydrophilic gelling agent with a specific polyethylene glycol, namely a polyethylene glycol in which the number of moles of oxyethylene 5 ranges from 12 to 180, it is possible to produce solid, homogeneous and stable aqueous gels which exhibit excellent cohesion and cleave easily under the finger or under the sponge, or else directly on the skin of the face or body.

10 In effect, the applicant has found that the combination of a polyethylene glycol in which the number of moles of oxyethylene is less than 12 with a hydrophilic gelling agent greatly decreases the hardness, which also makes cleavage virtually 15 impossible: the gel becomes too soft and the product can no longer be used as a stick or in a dish. Likewise, unexplainedly, the combination of a polyethylene glycol in which the number of moles of oxyethylene is greater than 180 with a hydrophilic 20 gelling agent also entails the softening of the gel, which, moreover, becomes sticky and is therefore not suitable for a cosmetic use. Only the combination claimed below, with a specific polyethylene glycol, makes it possible to obtain a solid composition which 25 has ideal properties both of cohesion and of cleaving.

The present invention therefore provides a solid aqueous gel comprising i) at least one

hydrophilic gelling agent and ii) at least one polyethylene glycol in which the number of moles of oxyethylene ranges from 12 to 180.

The gels of the invention exhibit excellent
5 cleaving and application qualities. In particular, by virtue of the combination according to the invention, a level of cleaving is obtained which is greater than that of the known sticks, at equivalent hardness. The product is easy to apply, and may be applied directly
10 to the body or with the finger or else by sponge, dispensing a sufficient quantity of product, which is easy to apply subsequently to the skin in a homogeneous manner without requiring wetting beforehand. The makeup obtained is uniform and homogeneous.

15 Moreover, these gels exhibit excellent cohesion. These gels are stable over time and with respect to temperature. Thus, after being kept at ambient temperature or at 45°C for two months, they exhibit no phenomenon of syneresis (exudation) or else
20 of phase separation; their appearance and their hardness are unchanged.

The gels according to the invention do not exude, even at low gelling agent contents, and they do not mandatorily necessitate the use of a particular
25 preparation technique. On application, they produce a sensation of great freshness while retaining good cosmetic properties, especially softness.

The present invention additionally provides a solid composition with a continuous aqueous phase comprising a gel as defined above.

The present invention further provides a
5 makeup product for the skin or keratinous fibers,
comprising a gel and/or a composition as defined above.

The present invention additionally provides a method of making up the skin and/or mucosae and/or keratinous fibers, which consists in applying to the
10 latter a solid aqueous gel and/or a solid composition and/or a makeup product as defined above.

In the context of the present invention,
solid composition or gel means a gel or composition having a hardness defined by a maximum force before
15 breakage which ranges from 5 to 50 grams at ambient temperature (20-25°C) following penetration by a stainless steel moving body 2 mm in diameter into the matrix of the gel or composition at a thickness of 1 mm at a rate of 1 mm/s and withdrawal of said moving body
20 from the matrix of the gel or composition at a rate of 2 mm/s, the maximum force before breakage being measured with a texture analyzer of the type "TAXT2"
25 sold by the company RHEO.

More preferably, the maximum force before
breakage ranges from 7 to 40 g.

The gel according to the invention comprises a hydrophilic gelling agent. By gelling agent is meant

a compound which, in the presence of a solvent, creates more or less strong intermacromolecular bonds, thereby giving rise to a three-dimensional network which entraps said solvent.

5 This hydrophilic gelling agent may be selected from polysaccharides, protein derivatives, synthetic or semisynthetic gels of polyester type, especially sulfonic type, polyacrylates or polymethacrylates and derivatives thereof.

10 Among the polysaccharides, mention may be made of:

- algal extracts such as agar, carragheenans (iota, kappa, lambda), alginates, especially those of Na or Ca;

15 - exudates of microorganisms, such as xanthan gum and its derivatives, such as the product sold under the trade name "Rheosan" by the company Rhodia Chimie, gellan,

- fruit extracts such as pectins;

20 - gelling agents of animal origin such as protein derivatives, especially gelatin, from cattle or fish, and caseinates;

- polysaccharides possessing a side chain and 6 neutral sugars, as described in the document FR-A-2759377,

25 - and mixtures thereof.

The synthetic or semisynthetic gels which may be mentioned include the copolyesters described in the application FR-A-2 760 643.

Preferably, the hydrophilic gelling agent is selected from the polysaccharides, and, more preferably, the hydrophilic gelling agent is gellan.

As products which are particularly suitable for the invention, mention may be made of the gellan gum sold under the trade name "Kelcogel F" by the company NUTRASWEET-KELCO or else the iota-carragheenan sold under the trade names "Seaspen PF 357" or "Viscarin SD 389" by the company FMC.

The hydrophilic gelling agent is present in the gel according to the invention at a concentration which makes it possible to obtain, in combination with specific polyethylene glycol, the hardness which is suitable for ideal cleaving. The hydrophilic gelling agent is preferably present in the gel according to the invention at a concentration which may range from 0.1 to 30%, more preferably from 0.2 to 10%, by weight, relative to the total weight of the gel.

The gel according to the invention also comprises a polyethylene glycol in which the number of moles of oxyethylene ranges from 12 to 180. Polyethylene glycols are known compounds of the following formula: $H(OCH_2CH_2)_nOH$, in which n represents the number of moles of oxyethylene. Compounds which can

be used in the present invention are, for example, the products listed in the CTFA under the names "PEG-12", "PEG-32", "PEG-75", "PEG-180". Mention may be made of the polyethylene glycol containing 12 EO sold under the
5 trade name "Polyéthylène 600" by the company Lambert Rivière, and the polyethylene glycol containing 180 EO sold under the trade name "Polyéthylène 6000" by the company Kao Soap.

Preferably, the polyethylene glycol which is
10 used in the present invention has a number of moles of oxyethylene of 12.

The polyethylene glycol according to the invention is present in the gel according to the invention at a concentration which makes it possible to
15 obtain, in combination with the hydrophilic gelling agent, the hardness and consistency which are suitable for ideal cleaving. Preferably, the polyethylene glycol according to the invention is present in the gel according to the invention at a concentration which may
20 range from 1 to 20% by weight, more preferably from 2 to 10% by weight, relative to the total weight of the gel.

The gels of the invention further comprise a cosmetically or physiologically acceptable medium,
25 i.e., a medium which is compatible with all of the keratinous matter such as the skin, nails, hair,

eyelashes and eyebrows, mucosae and semimucosae, and any other cutaneous zone of the body and of the face.

The gels according to the invention may further comprise a floral water such as cornflower 5 water and/or a mineral water such as VITTEL water, LUCAS water or LA ROCHE POSAY water and/or a thermal water.

The gels according to the invention may also comprise water-soluble dyes selected from the dyes 10 common in the field under consideration, such as Ponceau disodium salt, alizarin green disodium salt, quinoline yellow, amaranth trisodium salt, tartrazine disodium salt, rhodamine monosodium salt, fuchsin disodium salt and xanthophyll.

15 Preferably, the gels according to the invention comprise up to 98.9% by weight, preferably from 20 to 95% by weight, relative to the total weight of the gel, of water.

The gels according to the invention may 20 further comprise solvents other than water such as, for example, primary alcohols such as ethanol and isopropanol, glycols such as propylene glycol, butylene glycol, dipropylene glycol and diethylene glycol, glycol ethers such as the C₁-C₄ alkyl ethers of mono-, 25 di- or tripropylene glycol, mono-, di- or triethylene glycol, and mixtures thereof.

The rigidity of the gels according to the invention may be modified by admixing them with one or more salts which will increase this rigidity. These salts may be selected from mono-, di- or trivalent metal salts, and more particularly alkali metal and alkaline earth metal salts, and especially sodium, calcium or magnesium salts. The ions which make up these salts may be selected, for example, from carbonates, bicarbonates, sulfates, glycerophosphates, borates, chlorides, nitrates, acetates, hydroxides, persulfates and the salts of α -hydroxy acids (citrates, tartrates, lactates, malates) or fruit acids, or else the salts of amino acids (aspartate, arginate, glycocholate, fumarate). The amount of salt may range from 0.01 to 2% and preferably from 0.1 to 1% of the total weight of the gel.

Preferably, the salt is selected from calcium, magnesium or strontium nitrate, calcium or magnesium borate, calcium, sodium, magnesium, strontium, neodymium or manganese chloride, magnesium or calcium sulfate, calcium or magnesium acetate, and mixtures thereof. More preferably, the salt is magnesium chloride.

The gel according to the invention may also comprise a pulverulent phase which may comprise a pigment and/or a nacreous substance and/or a filler.

The term pigments should be understood as meaning white or colored, mineral or organic particles which are insoluble in the medium and which are intended for coloring and/or opacifying the
5 composition.

The pigments may be present in a proportion of 0-40% by weight relative to the total weight of the gel, preferably in a proportion of from 0.1 to 30% and more preferably in a proportion of 1-20%. They may be
10 white or colored, mineral and/or organic, of customary size or nanometric. Nanometric size refers to pigments whose average particle size ranges from 5 to 100 nm.

Among mineral pigments and nanopigments, mention may be made of titanium, zirconium or cerium
15 dioxides, and also zinc, iron or chromium oxides, nanotitaniums, and ferric blue. Among organic pigments, mention may be made of carbon black, and the lakes which are commonly employed to impart a makeup effect to the lips and to the skin, which are calcium, barium,
20 aluminum or zirconium salts of acid dyes such as halo-acid dyes, azo dyes or anthraquinonoid dyes.

The pigments may in particular be coated with silicone compounds such as PDMSSs and/or with polymers, especially polyethylenes, or else with fluorinated
25 compounds. Mention may thus be made of the Maprecos SA pigments or the Myoshi PI pigments.

The term nacreous substances is intended to embrace iridescent particles which reflect light.

The nacreous substances may be present in the gel in a proportion of 0-40% by weight, preferably in a 5 proportion of from 0.1 to 30% and more preferably in a proportion of 1-20% by weight.

Among the nacreous substances which may be considered, mention may be made of natural nacre, mica covered with titanium oxide, iron oxide, natural 10 pigment or bismuth oxychloride, and colored titanium mica.

By fillers are meant colorless or white, mineral or synthetic, lamellar or nonlamellar particles which are intended to give the composition body or 15 rigidity and/or the makeup softness, matteness and uniformity.

The fillers, which may be present in the gel in a proportion of 0-60% by weight relative to the total weight of the gel, preferably in a proportion of 20 from 0.1 to 40%, more preferably 1-20%, may be mineral or synthetic, lamellar or nonlamellar.

Mention may be made of talc, mica, silica, kaolin, powders of Nylon, poly- β -alanine and polyethylene, Teflon, lauroyl-lysine, starch, boron 25 nitride, bismuth oxychloride, tetrafluoroethylene polymer powders, polymethyl methacrylate powders, polyurethane powders, polystyrene powders, polyester

- powders, synthetic hollow microspheres, microsponges, silicone resin microbeads, oxides of zinc and of titanium, oxides of zirconium or of cerium, precipitated calcium carbonate, magnesium carbonate and
- 5 basic magnesium carbonate, hydroxyapatite, hollow silica microspheres, glass or ceramic microcapsules, metal soaps derived from organic carboxylic acids having 8 to 22 carbon atoms, preferably 12 to 18 carbon atoms, such as zinc stearate, magnesium stearate or
- 10 lithium stearate, zinc laurate and magnesium myristate, the compounds $\text{SiO}_2/\text{TiO}_2/\text{SiO}_2$, $\text{TiO}_2/\text{CeO}_2/\text{SiO}_2$, or else $\text{TiO}_2/\text{ZnO}/\text{talc}$, and polyethylene terephthalate/polymethacrylate polymers in the form of flakes.
- 15 Generally, the pulverulent phase comprises a sufficient amount of pigments and/or nacreous substances and/or fillers to provide the desired makeup effect. Preferably, therefore, the aqueous gel according to the invention is not transparent, i.e.,
- 20 the characters of a newspaper page cannot be seen through the gel. More preferably, it is not translucent, i.e., it does not allow the passage of light.

The gels of the invention may be incorporated

25 in cosmetic compositions, making up the continuous phase thereof. Such compositions may also comprise a fatty phase which may, for example, comprise an oil..

- Among the oils which may be used, mention may be made of oils of animal, vegetable or mineral origin, such as liquid paraffin, vaseline, perhydrosqualene, apricot oil, wheatgerm oil, sweet almond oil,
- 5 calophyllum oil, sesame oil, macadamia oil, grapeseed oil, colza oil, coprah oil, groundnut oil, palm oil, castor oil, avocado oil, jojoba oil, olive oil or cereal germ oil; esters of fatty acids and polyol, especially liquid triglycerides; alcohols;
- 10 acetylglycerides; octanoates, decanoates or ricinoleates of alcohols or polyalcohols; triglycerides of fatty acids; glycerides, fluorinated oils and perfluorinated oils; synthetic oils such as fatty esters; silicone oils such as volatile silicone oils,
- 15 polymethylsiloxanes, polymethylphenylsiloxanes, polysiloxanes modified with fatty acids, fatty alcohols or polyoxyalkylenes, fluorinated silicones and perfluorinated oils.

- The fatty phase of the compositions according
- 20 to the invention may further comprise other fatty substances, which may be selected by the skilled worker on the basis of his or her general knowledge such as to confer on the final composition the desired properties, in terms for example of consistency, texture and/or
- 25 transfer. These additional fatty substances may be waxes, gums and/or pastelike fatty substances of animal

origin, vegetable origin, mineral origin or synthetic origin, and mixtures thereof.

Mention may be made in particular of:

- silicone gums,
- 5 - waxes of animal, vegetable, mineral or synthetic origin such as microcrystalline waxes, paraffin, petrolatum, vaseline, ozokerite, montan wax; beeswax, lanolin and its derivatives; candelilla wax, ouricury wax, carnauba wax, Japan wax, cocoa butter, cork fiber
- 10 wax or sugarcane wax; hydrogenated oils which are solid at 25°C, ozokerites, fatty esters and glycerides which are solid at 25°C; polyethylene waxes and the waxes obtained by Fischer-Tropsch synthesis; hydrogenated oils which are solid at 25°C; lanolins; fatty esters
- 15 which are solid at 25°C; silicone waxes; fluorinated waxes; mixtures thereof.

The fatty phase may be present in proportions ranging, for example, up to 30%, preferably from 0.1 to 20% and, better still, from 0.5 to 10% of the total weight of the composition, these proportions varying depending on the selected application.

The oils or waxes may be introduced into the aqueous phase in the presence of one or more surfactants, in order to ensure a better dispersion.

25 The compositions according to the invention may therefore also comprise one or more ionic or nonionic O/W surfactants or cosurfactants, with a HLB

(hydrophilic/lipophilic balance) greater than or equal to 8, which are commonly used in the cosmetic field. When it is present, the amount of surfactant or cosurfactant ranges preferably from 0.05 to 8% of the 5 total weight of the composition.

The composition may further comprise any additional compound which is commonly used in the cosmetic field. These additional compounds may be selected from antioxidants, essential oils, 10 preservatives, active lipophilic or hydrophilic pharmaceutical or cosmetic substances, moisturizers, vitamins, essential fatty acids, sphingolipids, self-tanning compounds such as DHA, sunscreens, fragrances, and mixtures thereof.

15 The person skilled in the art will of course take care to select said optional additional compound(s), and/or the amount thereof, such that the advantageous properties of the gel and/or of the composition according to the invention are not, or not 20 substantially, adversely affected by the intended addition.

The gels and the compositions having a continuous aqueous phase, according to the invention, may be prepared in accordance with the conventional 25 methods of preparing sticks, these methods being well known to the person skilled in the art.

The gels and the compositions according to the invention may constitute products for making up or caring for the skin, in particular of the body, of the face and/or of the scalp, or of keratinous fibers,
5 especially the hair, nails, eyebrows and/or eyelashes, or else the mucosae, in particular the lips. They may therefore consistute body makeup products, foundations, eyeshadows, blushers, concealers, lipsticks, lipliner pencils, mascaras, eyeliner pencils, and sticks for
10 coloring or making up locks of hair.

The invention is illustrated in more detail in the examples below.

In the examples below, the amounts are given in percent by weight relative to the total weight of
15 the composition.

EXAMPLE 1:

The applicant has produced the aqueous gel in the form of the following stick foundation:

- Gellan gum sold under the trade name "Kelcogel F" by NUTRASWEET-KELCO	0.5%
- Mg chloride	0.1%
- PEG-12	5%
- Preservative	qs
- Pigments (iron oxides and titanium dioxide)	14%
- Propylene glycol	7%
- Water	qs 100%

This gel was prepared as follows: the water and the preservative were heated to 90°C, and then the gellan was incorporated with stirring. After waiting for 15 minutes, the MgCl₂ and PEG-12 were incorporated 5 with stirring, followed by the pigment paste, produced beforehand by mixing the pigments with the propylene glycol.

The mixture was subsequently poured into a dish and then cooled. The whole system is left to rest 10 at room temperature for 24 h.

The result is a stick which is very fresh on application, which is conveniently solid, is easy to pick up, and can be applied easily and homogeneously to the skin.

15 Making up the skin with such a stick gives a natural and transparent result, totally devoid of any greasy effect.

The hardness of this gel, measured as described above, is 19 g.

20 This stick cleaves very well.

EXAMPLE 2: Comparative

The applicant produced the same stick as in Example 1 but replacing the 5% of PEG-12 with 5% of PEG-8.

25 The stick obtained has a hardness, measured as described above, of 13.1 g.

This stick is too rubbery in texture to permit satisfactory cleaving.

EXAMPLE 3:

5 The applicant produced the same stick as in Example 1 but replacing the 5% of PEG-12 with 5% of PEG-180.

The stick obtained has a hardness, measured as described above, of 20.7 g;

10 It is easy to cleave. It permits homogeneous and uniform makeup directly on the skin, with the finger or with a sponge.

EXAMPLE 4: Comparative

15 The applicant produced the same stick as in Example 1 but replacing the 5% of PEG-12 with 5% of PEG-115M, in which the number of moles of oxyethylene is 115 000.

The stick obtained is extremely soft; its
20 hardness cannot be measured. This product is very sticky and is difficult to apply to the skin.